Texas Instruments Inc.

New Materials to Speed Signal Transfer in Integrated Circuits

In the mid-1990s, the U.S. semiconductor industry needed new manufacturing materials and techniques to keep pace with the trend toward miniaturization. Integrated circuits (ICs) had become so small that performance inefficiencies resulted because the aluminum interconnects had to be placed too closely together. A commonly used insulator that was placed between the interconnects was becoming ineffective as the miniaturization trend continued.

In 1994, Texas Instruments applied for and received Advanced Technology Program (ATP) funding to research two new materials, a polymer Teflon, and a special insulating material nanoporous silica, also known as aerogel, that could be used as interconnect materials. The goal of the project was to integrate these materials adjacent to on-chip interconnects in order to overcome problems with interconnect delay as a result of the continuing trend toward miniaturization. The project work started in 1995 when Texas Instruments subcontracted with a small company, NanoPore Corporation.

After three years of research funded by ATP, the two companies showed that aerogels held significant promise as an insulator for aluminum interconnect wiring. Furthermore, Texas Instruments and NanoPore developed the world's first fully automated manufacturing process to dry an aerogel quickly. The companies overcame impediments to aerogel processing early in the project, but in 1997, an industry competitor announced that it would begin using copper interconnect wiring in future IC designs. Texas Instruments then shifted focus away from aerogels for aluminum and began to develop copper interconnects. Before shifting focus, however, Texas Instruments transferred its aluminum circuit aerogel knowledge to NanoPore, which later sold the rights to continue development of the product to Honeywell. Honeywell's development efforts resulted in a product that they marketed briefly in 2002 to companies for use in manufacturing semiconductors. However, Honeywell withdrew the product in 2004 after it did not fulfill its potential as a new and innovative insulator.

COMPOSITE PERFORMANCE SCORE
(based on a four star rating)
* *

Research and data for Status Report 94-01-0221 were collected during January - February 2004.

Semiconductor Materials Reaching the Limit of Their Capabilities

In 1994, the U.S. semiconductor industry faced a crisis as the speed of signaling between different components within integrated circuits (ICs) approached the maximum speed enabled by IC materials. For a number of years, semiconductor transistors had been getting smaller without losing energy in the form of heat or power dissipation or without incurring "cross-talk" between different circuits as a result of capacitive "coupling" (signal merging). However, as semiconductor parts continued to get even smaller, signal delays between components on ICs were becoming greater. Furthermore, this technical problem was impeding improvements in devices such as digital signal processors, cell phones, and laptop computers.

On a semiconductor, metal interconnects of about 0.25-µm thickness conduct the signal/data between IC components. These interconnects need to be insulated from each other by materials called dielectrics. In the mid-1990s, the industry commonly used silicon dioxide (SiO_2) as the dielectric. However, as IC miniaturization progressed, increasing capacitance and resistance in the interconnect caused excessive signal delay.

(Resistance is a measure of how strongly an interconnect, such as one made of aluminum, supports electron or current flow. Capacitance is a measure of how much electrical charge a conducting material stores.) If there is too much resistance in an IC interconnect, then the circuit operation speed is too slow. If there is too much capacitance, then an unacceptable level of crosstalk occurs. Excessive resistance and capacitance are expressed as the “k” constant in the dielectric rating assigned by the industry standard. A lower k insulator material with a $k \leq 2$ was needed for semiconductors if miniaturization were to continue successfully. SiO_2 has a k of approximately 4, which translates to a serious performance bottleneck for the transmission speeds required in ICs. A new material with a k constant far lower than SiO_2’s needed to be developed.

Improved Dielectrics Would Mitigate the Signal Delay in ICs

Historically, the implementation of new materials in semiconductor processing has taken approximately a decade from concept to production. Texas Instruments subcontracted with NanoPore Corporation in 1995 to begin research into a new interconnect material; however, they faced difficulties in securing either internal or external funding. Therefore, Texas Instruments sought funding from ATP to develop and test two new dielectrics for aluminum leads, with the goal of determining which was better. Texas Instruments expected a reduction of up to 50 percent in power loss between components on ICs if a superior dielectric were found to replace SiO_2. Although copper is a better conductor, in the mid-1990s, aluminum was cheaper and less difficult to integrate with other IC components. If a lower k dielectric material could be developed, it would be another step in interconnect evolution towards the goal of approaching copper’s performance, without the difficulty of actually incorporating copper into semiconductor manufacturing.

Texas Instruments selected a special insulating material, silica aerogel, and an amorphous Teflon by DuPont, a polytetrafluoroethylene (PTFE) polymer, to test in separate testing regimens. These two materials were the lowest k materials available at the time. As dielectrics, both materials presented challenges in IC manufacturing. The aerogel required too much time to dry after application. The PTFE polymer would not adhere properly to other substances, which presented a problem in composing the multilayer design that is used in manufacturing ICs.

Aerogels or PTFEs: Which is Better?

Developed in 1931, an aerogel is a solid substance with air embedded in minute “pores” (in diameters of 10 to 20 nanometers, or 10 to 20 billionths of a meter). Air is the best dielectric known, but it must be encapsulated in another substance to be useful as a dielectric for IC interconnects. One of the lightest weight solids known, silica aerogel offers the following low-k dielectric properties:

- Thermal stability to 900ºC
- Small internal air pore size of 10 to 20 nanometers
- Controllable aerogel density during application (to vary the dielectric constant)
- Manufactured from silica, a substance widely used in the industry

Because the integration of aerogel with semiconductor components required extensive customization during the manufacturing process, it was more expensive to test than the Dupont Teflon material, PTFE. For example, a disadvantage of using an aerogel is its hydrophilic (water-absorbing) nature during and after deposition on a semiconductor. If it absorbs water, its pores collapse and the insulating properties are lost.

Furthermore, in 1994, the semiconductor industry was not capable of commercial mass-production of aerogel. The material required days to produce, which was significantly longer than the seconds or minutes required for commercial acceptance. Aerogel production also required that scientists spend significant time in a wet lab to complete production. Moreover, modeling showed that aerogels would not adhere to aluminum semiconductor circuits. A new type of aerogel would need to be developed before the material could be used in semiconductors.

The other dielectric that was tested, the polymer Teflon, has the lowest dielectric constant of any plastic material (1.9 to 3.9). It is chemically inert and is compatible with most IC manufacturing techniques. Teflon is applied using a dry application technique (dry etch), a procedure that is different from the wet application used with aerogel. When the application is complete, a Teflon-coated surface is hydrophobic (water-resistant).

However, this hydrophobic property often presents adhesion problems when other materials need to be added on top of the Teflon layer.

Aerogels Demonstrate Early Superiority

The improved properties that NanoPore and Texas Instruments sought for aerogels included the following: higher mechanical strength, better dimensional stability, higher thermal stability, better ability to etch small circuits onto the materials, lower degree of moisture absorption, better adhesion, higher thermal conductivity, lower leakage of current, and lower overall cost. No dielectric has all these properties, so achieving the desired improvements required radical rethinking of aerogel's manufacturing and use. The biggest drawback of aerogels was the long drying time needed. ATP funding enabled the test team to start with the technically riskier aerogel materials. As the PTFE was easier to work with, the team decided to do the more difficult task first (the aerogels).

Texas Instruments and NanoPore identified four tasks for this three-year project:

- Evaluating a thin-film aerogel
- Designing tests for the amorphous Teflon and the silica aerogel
- Testing Teflon with several layers of IC structures
- Device modeling at Texas Instrument's Semiconductor Process and Device Center

The team achieved early success with aerogel and discovered that aerogel adhesion layer combinations could insulate aluminum semiconductor wiring. The aerogel tests went so well that the companies were able to shorten their original test schedule by three years. However, less success was achieved with Teflon. Texas Instruments determined that Teflon was a poor choice as an interlevel dielectric material; adhering it to the semiconductor made overlaying additional circuits extremely difficult. Subsequently, Texas Instruments switched to a different PTFE supplied by W.L. Gore. Even though Gore's PTFE showed promising results, it failed to demonstrate the ability to reduce capacitance. Moreover, it had leakage, delamination, and dispersion problems. Therefore, in the final year of the project, Texas Instruments decided, on the basis of test results, not to pursue PTFE development unless W.L. Gore improved the material.

Aerogel Deposition Problems Solved

During the first year of the ATP-funded project, the team was able to reduce aerogel production time from 90 to 20 minutes; however, 20 minutes was still 10 times too long for commercial acceptance. Later the team discovered that by using ethylene glycol in the aging phase of the gel processing, they could reduce the production process to 1 to 2 minutes, which was acceptable for competitive manufacturing. As the aerogel was drying much faster, engineers called it an "xerogel," (literally, a "dried" gel). Texas Instruments and NanoPore worked with two vendors to develop the world's first fully automated xerogel processing tool, which used a new solvent that quickened the drying time. The tool, which Texas Instruments paid approximately $1 million of its own funds to create, was installed in 1997. As a result, the processing tool enabled 1- to 2-minute xerogel production and replaced the previous 20-minute process.

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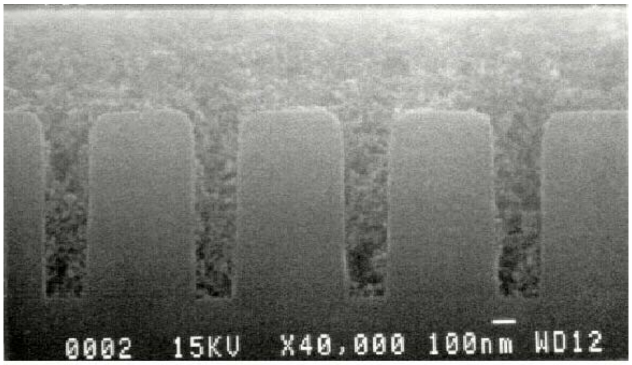
The companies continued working to bring xerogels into the market. They also worked with SEMATECH, the semiconductor industry trade association, to make xerogels available for all American semiconductor industry participants. However, at the same time, in late 1997, IBM introduced copper wiring into semiconductor circuits by developing a process that prevented the copper from leaching into the silicon layer; before this, copper had been too difficult to use. This breakthrough caused Texas Instruments to change its focus from xerogels with aluminum circuits to developing copper wiring. The company transferred its knowledge about xerogels for aluminum wiring to NanoPore.

At the conclusion of the ATP-funded project, xerogel was a pre-commercial prototype and would still require years of development. NanoPore and AlliedSignal formed a 50/50 joint venture called Nanoglass LLC and worked together to further develop the material into a product they called NANOGLASS (see Figure 1). Then AlliedSignal and Honeywell merged, and Honeywell bought NanoPore's stake in the product. AlliedSignal changed the name of the xerogel to NANOGLASS E and entered into research collaboration with General Electric and Armstrong to explore the use of xerogels as a heat insulator in other, non-semiconductor applications.



NANOGLASS™ gapfill: 0.15 micron, 6:1 aspect ratio

Figure 1. Cross section scanning electron micrograph of the dielectric insulator NANOGLASS filling the gaps between aluminum interconnects. The "bubbly" appearance of the NANOGLASS is due to embedded air.

Currently, as market pressures dictate that circuits continue to grow smaller and faster, copper wiring is the clear choice for use in semiconductors. At some point in the near future, however, the dielectrics in use today will be obsolete due to the trend toward miniaturization. To address this eventuality, many in the semiconductor industry, including Honeywell, Texas Instruments, NanoPore, and other semiconductor companies, have refocused on xerogels to try to adapt them for use with copper wiring. As of 2004, due to poor sales, Honeywell abandoned the NANOGLASS E material that it sold briefly as a manufacturing material for semiconductor insulators.

Team Shared Project Knowledge

Texas Instruments and NanoPore published their project-related information in two professional journals, gave presentations at a number of industry conferences, and disclosed knowledge they learned from this ATP-funded project in 24 patents. In addition, some knowledge from the project was disseminated to suppliers such as AlliedSignal, DuPont, and W.L. Gore.

Conclusion

Texas Instruments and NanoPore tested polymers and aerogels in order to develop a new material that could be used in semiconductors to reduce crosstalk and to improve transmission speed. The aerogel product demonstrated early superiority, while the polymer development process for use in semiconductors was fraught with problems and was eventually abandoned.

After the partners discovered a process to apply and dry aerogel at a commercially acceptable speed, a new aerogel called xerogel was created. At the conclusion of the ATP-funded project, their teaming arrangement grew into a joint venture that produced a product, NANOGLASS, which was later purchased and refined into NANOGLASS E by Honeywell. The company sold this product briefly for use as a dielectric with copper interconnects and nonsemiconductor applications. By 2004, however, Honeywell discontinued selling the material due to poor sales.

PROJECT HIGHLIGHTS
Texas Instruments Inc.

Project Title: New Materials to Speed Signal Transfer in Integrated Circuits

Project: To integrate new dielectric materials (amorphous Teflon or silicon-dioxide-based xerogel) adjacent to on-chip interconnects in order to overcome problems with interconnect delay as a result of the continuing trend toward miniaturization.

Duration: 3/1/1995 - 2/28/1998
ATP Number: 94-01-0221

Funding (in thousands):**

ATP Final Cost	$1,629	37%
Participant Final Cost	$2,742	63%
Total	$4,371	

Accomplishments: With ATP funding, Texas Instruments accomplished the following:

- Generated a large amount of information on the use of aerogels to insulate aluminum semiconductor wiring.
- Developed and put in production the world's first fully automated aerogel processing system. The system enabled certain types of aerogels, known as xerogels, to be produced in 1 to 2 minutes rather than the typical 90 minutes.

NanoPore continued to develop xerogels for use with aluminum semiconductor wiring, first through a agreement with Texas Instruments and then by teaming with AlliedSignal. Currently, several semiconductor companies are selling xerogel materials for integrated circuits (IC) dielectrics. Even though the semiconductor industry is moving toward copper wiring, Texas Instruments and NanoPore's xerogel research will have future applications.

Texas Instruments and NanoPore representatives delivered presentations on the ATP-funded technology at a number of conferences between 1995 and 1997 and published two papers in the MRS Bulletin in 1997. In addition, Texas Instruments received the following 24 patents for technologies related to the ATP-funded project:

- "Porous dielectric material with improved pore surface properties for electronics applications" (No. 5,523,615: filed June 7, 1995, granted June 4, 1996)
- "Porous composites as a low dielectric constant material for electronics applications" (No. 5,561,318: filed June 7, 1995, granted October 1, 1996)
- "Porous dielectric material with improved pore surface properties for electronics applications" (No. 5,723,368: filed June 7, 1995, granted March 3, 1998)
- "Low dielectric constant material for electronics applications" (No. 5,789,819: filed June 7, 1995, granted August 4, 1998)
- "Method of making a low dielectric constant material for electronics" (No. 5,804,508: filed October 23, 1996, granted September 8, 1998)
- "Glycol-based method for forming a thin-film nanoporous dielectric" (No. 5,736,425: filed November 14, 1996, granted April 7, 1998)
- "Rapid aging technique for aerogel thin films" (No. 5,753,305: filed November 14, 1996, granted May 19, 1998)
- "Polyol-based method for forming thin film aerogels on semiconductor substrates" (No. 5,807,607: filed November 14, 1996, granted September 15, 1998)
- "Porous dielectric material with improved pore surface properties for electronics applications" (No. 5,847,443: filed November 14, 1996, granted December 8, 1998)
- "Low volatility solvent-based method for forming thin film nanoporous aerogels on semiconductor substrates" (No. 5,955,140: filed November 14, 1996, granted September 21, 1999)
- "Limited-volume apparatus and method for forming thin film aerogels on semiconductor substrates" (No. 6,037,277: filed November 14, 1996, granted March 14, 2000)

** As of December 9, 1997, large single applicant firms are required to pay 60% of all ATP project costs. Prior to this date, single applicant firms, regardless of size, were required to pay indirect costs.

PROJECT HIGHLIGHTS
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- “Nanoporous dielectric thin film surface modification”
(No. 6,063,714: filed November 14, 1996, granted May 16, 2000)

- “Aerogel thin film formation from multi-solvent systems”
(No. 6,130,152: filed November 14, 1996, granted October 10, 2000)

- “Stress relief matrix for integrated circuit packaging”
(No. 5,894,173: filed November 5, 1997, granted April 13, 1999)

- “Metallization method for porous dielectrics”
(No. 6,156,651: filed December 10, 1997, granted December 5, 2000)

- “Integrated circuit dielectrics”
(No. 6,059,553: filed December 17, 1997, granted May 9, 2000)

- “Porous dielectric material with improved pore surface properties for electronics applications”
(No. 6,140,252: filed May 5, 1998, granted October 31, 2000)

- “Integrated circuit dielectric and method”
(No. 6,008,540: filed May 28, 1998, granted December 28, 1999)

- “Integrated circuit dielectric and method”
(No. 6,351,039: filed May 28, 1998, granted February 26, 2002)

- “Polyol-based method for forming thin film aerogels on semiconductor substrates”
(No. 6,171,645: filed July 15, 1998, granted January 9, 2001)

- “Stress relief matrix for integrated circuit packaging”
(No. 6,096,578: filed January 21, 1999, granted August 1, 2000)

- “Integrated circuit dielectric and method”
(No. 6,265,303: filed November 9, 1999, granted July 24, 2001)

- “Nanoporous dielectric thin film formation using a post-deposition catalyst”
(No. 6,319,852: filed January 20, 2000, granted November 20, 2001)

- “Aerogel thin film formation from multi-solvent systems”
(No. 6,437,007: filed April 14, 2000, granted August 20, 2002)

Commercialization Status: In 2001, NANOGLASS LLC, a subsidiary of Honeywell and formerly a 50/50 joint venture between Honeywell/AlliedSignal and NanoPore, successfully integrated copper and NANOGLASS xerogel. This material for manufacturing was sold briefly as NANOGLASS E. Its development is directly traceable to the ATP-funded research performed during this project. As of 2004, the product is no longer offered due to poor sales.

Outlook: The outlook for the product developed during this project remains weak. Although the project succeeded technically, the technology was surpassed in the second year of the project by competing technology that uses copper instead of aluminum. The ATP-funded technology has been transferred to Honeywell, which sold it briefly as a dielectric material for use with manufacturing semiconductor interconnects of copper.

Composite Performance Score: * *

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Publications: Company representatives published the following articles related to the project research:

- Jin, Changming, J.D. Luttmer, Douglas M. Smith, and Teresa A. Ramos. “Nanoporous Silica As An Ultralow-k Dielectric,” MRS Bulletin, 22:10, 61, 1997.

- List, R. Scott, Abha Singh, Andrew Ralston, and Girish Dixit. “Integration of Low-k Dielectric Materials Into Sub-0.25-μm Interconnects,” MRS Bulletin, 22:10, 61, 1997.